

# NO<sub>x</sub> storage-reduction catalysts for gasoline engines

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The automotive catalyst technology is now faced with very difficult problems. As the result of automakers' efforts to produce more efficient and lower-emission vehicles, lean-burn gasoline engines have been introduced into the market. While these engines are much more efficient than conventional ones, NO<sub>x</sub> removal has become significantly more difficult. After enormous efforts, we succeeded in solving the problem, by inventing a new class of catalyst. We overcame two strict problems with the new type catalyst, which are sulfur poisoning and thermal deterioration.

We have improved the support type and reformed the steam and substrate qualities by clarifying the related degradation mechanisms.

Here our challenges to develop a new catalyst to store and then reduce NO<sub>x</sub> are described. The catalyst has made it possible to make emissions of lean-burn engines meet strict NO<sub>x</sub> regulations.

**KEY WORDS:** NO<sub>x</sub> storage-reduction catalyst; sulfur poisoning; direct injection gasoline engine; steam reforming; hexagonal cell monolithic substrate

## 1. Introduction

For the protection of global environment, automakers have been struggling to suppress the carbon dioxide emission, and at the same time, to clean up automobile exhaust gases. Also, a new generation of engine technology has placed severe demands on the catalyst. Lean-burn engine technology, which has been featured in vehicles since 1984, forces engine combustion to occur at very high air–fuel ratios. The normal 14.5:1 (stoichiometric) ratio produces exhaust gas that contains properly balanced CO, H<sub>2</sub> and HC to reduce NO<sub>x</sub> and O<sub>2</sub>. Lean-burn engines, which operate at air–fuel (A/F) ratios of 25:1 and above, effectively improve the fuel economy of gasoline-engine vehicles, but produce oxygen-rich exhaust gases (figure 1). Removal of NO<sub>x</sub> from oxygen-rich exhaust with the conventional three-way catalyst has been extremely difficult. As a result, the engine has to be operated in a very narrow lean-burn zone, which is the major obstacle in fuel economy improvement. This situation has prompted the research on the development of a new catalyst technology that is capable of reducing NO<sub>x</sub> in excess oxygen, which is called the NO<sub>x</sub> storage-reduction (NSR) catalyst. Recently, catalysts for selective NO<sub>x</sub> reduction by hydrocarbons in an oxidizing atmosphere have been extensively studied [1–7]. These catalysts, however, have several serious problems such as low catalytic activities, narrow temperature-windows, insufficient durability and so on [8]. Therefore, they have not been applicable practically as automotive catalysts.

This paper reviews past development activities concerning the NO<sub>x</sub> catalyst for gasoline engines.

## 2. Discovery and mechanism of NO<sub>x</sub> storage reduction mechanism

With regard to lean-burn engines operated with three-way catalyst containing acidic substance as a catalytic component, it has been found that the NO<sub>x</sub> reduction rate is much better under the condition repeating acceleration and deceleration as during street traveling than during ordinary traveling. Figure 2 shows the measured NO<sub>x</sub> concentrations before and after the catalyst when the engine is operated alternatively at lean-burn ratio (A/F = 18) and at stoichiometric ratio (A/F = 14.6) at intervals of 2 min. At an A/F of 14.6, all of three components (HC, CO and NO<sub>x</sub>) were removed almost 100%. For about 1 min after A/F switching to 18, NO<sub>x</sub> reduction rate remain unchanged. The NO<sub>x</sub> reduction rate drops gradually after lapse of about 1 min, but it was recovered to about 100% after A/F switching again to 14.6. This phenomenon was reversible invariably for several repeated cycles. We have developed the NO<sub>x</sub> storage-reduction catalyst based on this newly discovered principle.

### 2.1. Mechanism

This storage-reduction procedure in a two-step cycle has been proved to be very promising. During the lean-burn stage, excess NO<sub>x</sub> is oxidized by oxygen and stored in the form of nitrate (NO<sub>3</sub><sup>−</sup>) in a barium-based storage material as described below. Thanks to ample oxygen present in this stage, HC, H<sub>2</sub>, and CO are readily oxidized into water and carbon dioxide. When the engine is switched to operation with the normal air–fuel mixture, the resulting exhaust becomes comparatively oxygen-deficient then HC, H<sub>2</sub>, and CO remains without oxidation. So these components react with the NO<sub>3</sub><sup>−</sup>

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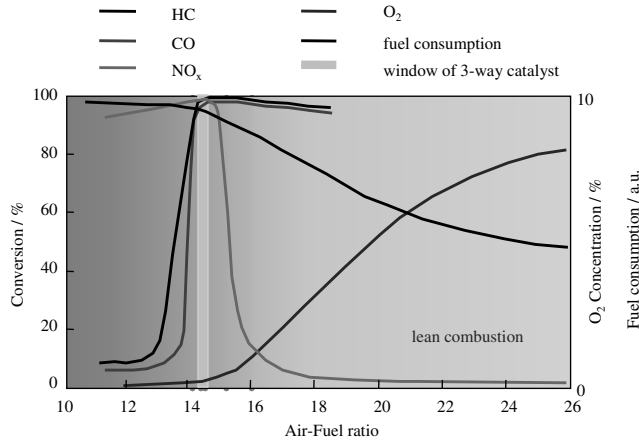


Figure 1. Fuel consumption and three-way performance of a gasoline engine as a function of air-fuel(A/F) ratio.

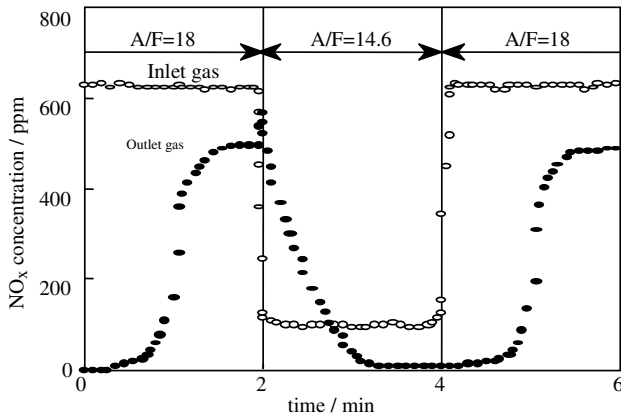
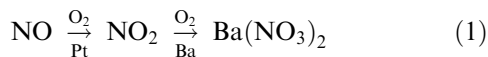


Figure 2. Transient NO<sub>x</sub> conversion phenomenon on Pt/Rh/La<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst.

stored in the catalyst. These reactions reduce NO<sub>3</sub><sup>-</sup> into harmless nitrogen, water, and carbon dioxide (figure 3). This is a novel concept called NO<sub>x</sub> storage-reduction. The first NSR catalyst was developed and put into the market by Toyota in 1994 [9,10].

We confirmed the storage-reduction mechanism catalyzed by Pt-Ba/Al<sub>2</sub>O<sub>3</sub> [11]. In the oxygen-rich atmosphere, NO<sub>x</sub> is oxidized by oxygen and then stored as Ba(NO<sub>3</sub>)<sub>2</sub> by means of the following mechanism:



The importance of the first step is evident from the fact that NO is not stored in the catalyst without oxygen. The nitrogen species stored in the catalyst is identified as nitrate by IR spectroscopy [11].

In the oxygen-deficient atmosphere, where HC, H<sub>2</sub>, and CO are present in excess, Ba(NO<sub>3</sub>)<sub>2</sub> is reduced to N<sub>2</sub> and BaCO<sub>3</sub> by the following mechanism:

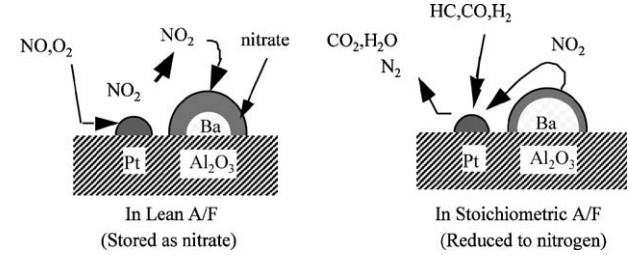
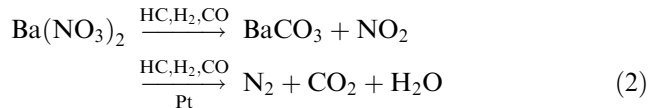


Figure 3. Possible mechanism of the NO<sub>x</sub> storage-reduction on the NSR catalyst.



The first step does not occur in the He atmosphere, without HC, H<sub>2</sub>, and CO, at 673 K, which is the normal temperature for using an automotive catalyst. When the atmosphere switches to a reducing mixture such as He and N<sub>2</sub> with H<sub>2</sub>, N<sub>2</sub> was the only nitrogen species detected by mass-spectroscopy at the outlet [11].

### 3. Composition of NO<sub>x</sub> Storage Reduction (NSR) catalyst

The NSR catalyst is constructed similarly as the ordinary three-way catalyst. A honeycomb substrate is coated with the support (oxides) that has a high specific surface area. Both NO<sub>x</sub> storage materials consist of alkaline-earth metals or alkaline metals and noble metals such as platinum and rhodium reside dispersed on the surface of the support. As the basicity of NO<sub>x</sub> storage materials gets stronger, the amount of NO<sub>x</sub> that can be stored (figure 4) increases. Furthermore in the high temperature range at 400 °C or above, the NO<sub>x</sub> storage temperature and amount vary with the type of the storage material. Figure 5 shows the temperature characteristics of the NO<sub>x</sub> storage amount of two types

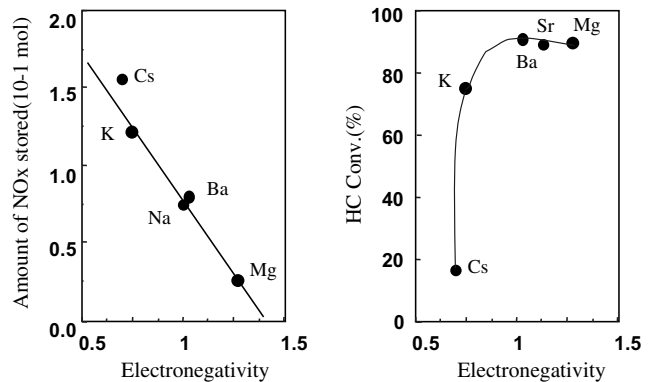


Figure 4. Amounts of NO<sub>x</sub> storage and HC conversion of alkali, alkaline earth added catalysts. Catalyst: Pt/M/Al<sub>2</sub>O<sub>3</sub> M = Mg, Ba, Sr, Na, K, Cs. Temperature: Amount of NO<sub>x</sub> stored at 300 °C (HC purification rate is for 10–15 mode.).

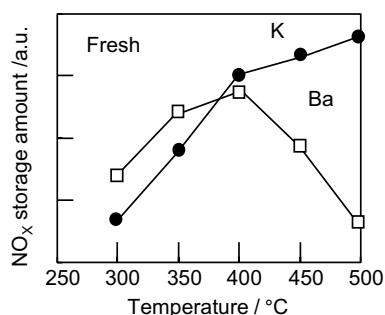


Figure 5. NO<sub>x</sub> storage properties of catalysts composed of K or Ba. Catalyst: Pt/K or Ba/gamma-Al<sub>2</sub>O<sub>3</sub>.

of catalysts, each containing barium or potassium as the storage material.

However, HC conversion decreases in the presence of a strongly basic alkaline element. We have, therefore, concluded that barium and potassium are the most suitable elements of the NSR catalyst.

#### 4. Degradation mechanism and improvement

Although numerous experimental investigations on the NSR catalyst have been conducted and theoretical models for this reaction have been developed [12–19], problems still remain mainly with respect to deactivation of the catalysts.

Deactivation caused by sulfur is one of the most difficult problems with the NSR catalyst that has to be solved. Another serious problem is thermal deterioration due to the reaction of NO<sub>x</sub> storage material with compounds in the wash-coat and to the particle growth of both the precious metals and the NO<sub>x</sub> storage material [20].

##### 4.1. Poisoning mechanism of NSR catalyst

Sulfur oxides (SO<sub>x</sub>) in exhaust gas react on the catalyst in the same way as NO<sub>x</sub>. The SO<sub>x</sub> species in automobile exhaust gas is almost exclusively SO<sub>2</sub>, which derives from the combustion of sulfur compounds in fuel. Figure 6

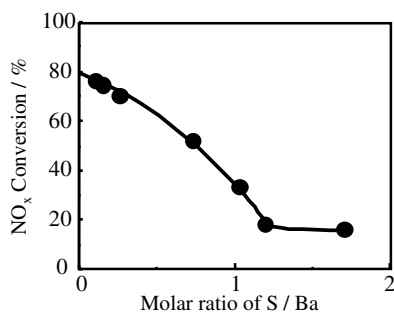


Figure 6. Relationship between the efficiency of NO<sub>x</sub> conversion and the amount of sulfur deposit on the catalyst after durability test. Catalyst: Pt/Ba/gamma-Al<sub>2</sub>O<sub>3</sub>.

shows the relationship between the NO<sub>x</sub> conversion and the amount of sulfur deposited on the NSR catalysts after durability tests by using fuel with certain sulfur content. The NO<sub>x</sub> conversion decreased with an increase in the sulfur to barium ratio. Sulfate species were detected by FT-IR spectroscopy and BaSO<sub>4</sub> was identified by XRD on the catalyst after the durability test. On the basis of these facts together with the thermogravimetric analysis of the catalyst poisoned by sulfur, we assumed that there are two types for the causes of sulfur poisoning of NSR catalyst as described below [21]:

- (1) SO<sub>2</sub> in the exhaust gas is oxidized on precious metals, and then reacts with alumina (γ-Al<sub>2</sub>O<sub>3</sub>) to form aluminum sulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>). Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> covers the surface of γ-Al<sub>2</sub>O<sub>3</sub> or plugs the micro-pores of γ-Al<sub>2</sub>O<sub>3</sub>.
- (2) SO<sub>x</sub> reacts with the NO<sub>x</sub> storage components to form barium sulfate (BaSO<sub>4</sub>). Since sulfates are more stable than nitrates, once the storage compound has reacted to form BaSO<sub>4</sub>, it is no longer available to react with NO<sub>x</sub>. As time passes, NO<sub>x</sub> storage capacity gradually drops, and the catalyst loses activity.

##### 4.1.1. Influences of supports on sulfur poisoning

Titanium oxide (TiO<sub>2</sub>) is the most promising candidate for the support to overcome sulfur poisoning. A small amount of TiO<sub>2</sub> added to the alumina catalyst coating reduces the amount of sulfate stored and suppresses the size of the sulfate particles formed, without reducing much the NO<sub>x</sub> storage capacity. The size issue is important: the smaller the size of the sulfate particles, the more easily they are removed from the catalyst under reducing conditions (i.e., when the engine is operated at a normal air–fuel ratio).

Finer TiO<sub>2</sub> particles will improve the contact between TiO<sub>2</sub> and sulfate to accelerate sulfate decomposition.

##### 4.1.2. Desorption of sulfur from poisoned catalyst by stream reforming reaction

Figure 7 shows the relationship between the kind of reducing gases and the elimination of H<sub>2</sub>S from the aged

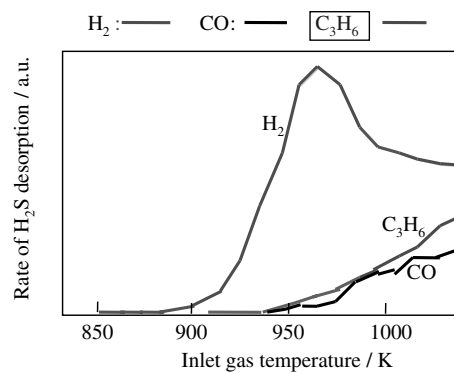
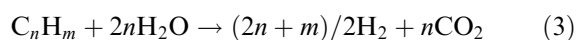


Figure 7. Relationship between the kind of reducing gases and the desorption characteristics of H<sub>2</sub>S. Catalyst: Pt/Rh/Ba/gamma-Al<sub>2</sub>O<sub>3</sub> after the sulfur poisoning test under the lean atmosphere at 873 K.

catalysts ( $\text{Pt/Rh/Ba}/\gamma\text{-Al}_2\text{O}_3$ ) after the sulfur-poisoning test under the alternate lean-rich gas conditions. In a hydrogen flow, the elimination of  $\text{H}_2\text{S}$  was prominent when the temperature reached approximately 873 K. In a propane or carbon monoxide flow, on the other hand, the elimination of  $\text{H}_2\text{S}$  was observed at temperatures only above 923 K, and the amount of  $\text{H}_2\text{S}$  eliminated was much smaller.

We designed a catalyst that promotes the decomposition of sulfate by hydrogen formed in the vicinity of the  $\text{NO}_x$  storage element as described below. Automobile exhaust gas contains about 10% water vapor. We focused on steam reforming reaction (equation (3)), in which hydrogen is formed by the reaction of hydrocarbon, which is usually contained at about 0.5% carbon basis in automobile exhaust gas, with water vapor on the catalyst.



Rhodium loaded on  $\text{ZrO}_2$  provided the highest catalytic activity for steam reforming reaction (figure 8). We evaluated the amount of hydrogen formed on NSR catalyst with  $\text{Rh}/\text{ZrO}_2$  ( $\text{Rh}/\text{ZrO}_2$ -added catalyst), and confirmed that this catalyst has high activity for hydrogen generation.

Addition of Ca, etc. to the  $\text{ZrO}_2$  support increases the basic hydroxyl group to increase  $\text{H}_2\text{O}$  adsorption for better  $\text{H}_2$  generation performance of the  $\text{Rh}/\text{reformed-ZrO}_2$ . As a result, the sulfur resistance of the catalyst is improved greatly [22].

#### 4.1.3. Effects of the structures of substrates on sulfur desorption

Removal of sulfur from the catalyst is more difficult in portions where the alumina coating is thick (i.e., thicker than about  $100\text{ }\mu\text{m}$ ) [23]. Conventional catalytic converters have square-shaped cells for the structure of catalyst support. When the alumina coating is applied to the square cells, it builds up to a much greater thickness at the corners, making the sulfur removal significantly more difficult.

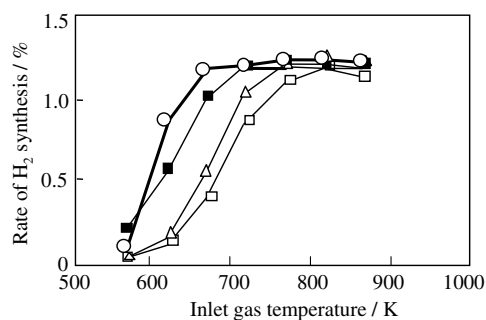


Figure 8. Formation of hydrogen on several catalysts under a flow of rich gas ( $\text{A}/\text{F}=12$ ). (○)  $\text{Rh}/\text{ZrO}_2$ ; (△)  $\text{Pt}/\text{ZrO}_2$ ; (■)  $\text{Rh}/\text{Al}_2\text{O}_3$ ; (□)  $\text{Rh}/\text{TiO}_2$ .

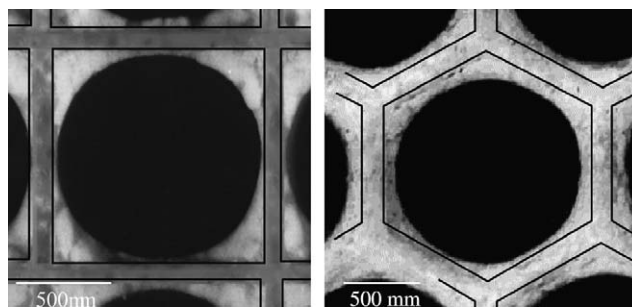


Figure 9. Photographs of wash-coat layer on square-cell(left) and hexagonal-cell(right) monolithic substrate.

Catalysts currently in use for automobile exhaust treatment employ ceramic monolithic substrate having square cells. When wash-coat slurry is applied to this substrate, the shape of the cell void becomes round, as shown in figure 9 (left), due to the surface tension of the slurry. In other words, the wash-coat is thinner on flat side of the cell, and much thicker at the corner. The wash-coat is approximately  $20\text{ }\mu\text{m}$  thick at the flat side and  $250\text{ }\mu\text{m}$  thick at the corner. A decrease in the amount of wash-coat brings about uniform thickness of wash-coat, but the deterioration of catalytic performance by the sulfur poisoning is accelerated [9]. Therefore, for effective use of the catalytic components to promote sulfur elimination, the wash-coat thickness must be uniform to distribute the catalytic components uniformly to the appropriate depth.

Figure 9 (right) is a photograph showing a coated catalyst with a hexagonal cell substrate. The amount of wash-coat on this substrate is the same as that on the square cell substrate (figure 9, left). Clearly, the wash-coat thickness varies much less for the hexagonal cell substrate than for the square cell substrate. The fraction of wash-coat less than  $100\text{ }\mu\text{m}$  thick is about 90% for the hexagonal cell, compared with about 66% for the square cell, the thickness being almost uniform for the former.

To ascertain the effect of cell structure on the sulfur desorption, we measured the sulfur desorption under a rich atmosphere for 5 s, after being treated in a lean atmosphere for 60 s. The amount of  $\text{H}_2\text{S}$  desorbed from the catalyst with the hexagonal cell substrate was more

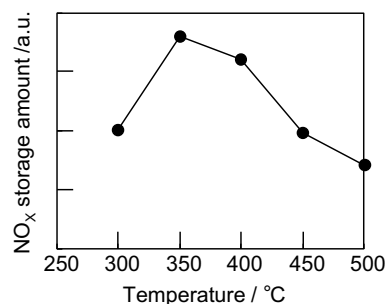


Figure 10.  $\text{NO}_x$  storage properties of  $\text{Pt/Rh/Ba/K}/(\text{Al}_2\text{O}_3 + \text{TiO}_2)$  after durability test.

Table 1  
Specific surface area and amount of NO<sub>x</sub> storage after durability test

	SSA <sup>a</sup>	NO <sub>x</sub> storage amount <sup>a</sup>
Pt/K/(Al <sub>2</sub> O <sub>3</sub> + TiO <sub>2</sub> )	1	1
Pt/K/(Al <sub>2</sub> O <sub>3</sub> + ZrO <sub>2</sub> + TiO <sub>2</sub> )	1.1	2.9

<sup>a</sup>Normalized by data of Pt/K/Ba/(Al<sub>2</sub>O<sub>3</sub> + TiO<sub>2</sub>). Sample: pellet catalyst. Aging condition: SSA 800 °C 10 h in air. NO<sub>x</sub> storage A/F = 22(55 s)–A/F = 12(5 s), 800 °C.

than twice that of the square cell substrates [23]. After an engine durability test, the amount of NO<sub>x</sub> storage and SO<sub>x</sub> deposit was measured as well. This revealed that the hexagonal cell substrate had approximately 20% higher NO<sub>x</sub> storage, and substantially lower SO<sub>x</sub> deposit than the square cell substrate.

#### 4.2. Thermal deterioration

Figure 10 shows the amount of NO<sub>x</sub> storage after the durability test of the catalyst containing both barium and potassium as storage materials. A catalyst coated on 1.3 dm<sup>3</sup> of cordierite monolith substratum was used. We conducted a durability test by simulating street traveling by using a D-4 engine with a displacement of 2.0 dm<sup>3</sup> and gasoline with much sulfur content (S = 200 ppm). Figures 5 and 10 shows degradation of potassium characteristic in the high temperature zone after the durability test. Potassium degradation may have been the major cause of degradation in the high temperature zone in figure 10.

A study using temperature program desorption – MASS and XRD has clarified high thermal stability of KNO<sub>3</sub> loaded on ZrO<sub>2</sub> support and low thermal stability of that loaded on TiO<sub>2</sub> support.

This tells that potassium degradation at high temperatures results from lowering of KNO<sub>3</sub> thermal stability by the interaction with the TiO<sub>2</sub> support and inactivation of potassium by solid layer reaction with the support [24].

With regard to the thermal stability of KNO<sub>3</sub> and resistance to sulfur poisoning, compounding TiO<sub>2</sub> excellent in thermal stability and ZrO<sub>2</sub> ensuring thermal stability of KNO<sub>3</sub> will improve the thermal stability of KNO<sub>3</sub> while maintaining the acidity of the support effective against sulfur poisoning and improve the thermal stability of the support to suppress solid reaction with potassium (table 1) [24].

Balanced compounding of the support effective for sulfur resistance and the support effective against thermal degradation is an important factor in improving the durability of practical catalysts.

#### 5. Summary and future study themes

Analysis of the reaction mechanism of the NSR catalyst discovered from NO<sub>x</sub> removal phenomenon in lean atmosphere during repeated lean-stoichiometric switching operation has revealed a higher-efficiency

material, which has been put into practical use since 1994.

In the reaction mechanism of the NSR catalyst, NO is oxidized into nitric salts in the excess oxygen state and stored by alkaline metals and alkaline-earth metals such as barium and potassium as NO<sub>x</sub> storage materials. Reduction into harmless substances by the reduction agents in the exhaust gas occurs when the engine is switched to the normal running state.

One of NSR catalyst degrading causes is catalyst poisoning by sulfur in the fuel. Improvement has been made by the effectiveness of TiO<sub>2</sub> support to free sulfur, use of water vapor reforming reaction and adoption of new substrate structure.

Thermal degradation as another cause is found to result from the interaction between potassium as the NO<sub>x</sub> storage material and the support. ZrO<sub>2</sub> support is found effective to solve this problem.

Further improvement of the catalyst performance is necessary to satisfy strengthening exhaust emission control in the future. Much improvement against sulfur poisoning is also necessary to handle various types of fuel used in different countries worldwide.

In addition to wider studies regarding catalyst materials and reactions, studies on dynamic reactions and degradation phenomena with sufficient consideration of catalyst use conditions in the development example introduced here and comprehensive technological development for the entire vehicle system will become more important.

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